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ScienceDirect

Procedia Chemistry 20 (2016) 118 – 120

Procedia Chemistry

11th Asian Conference on Chemical Sensors, ACCS 2015

Selective CO detection using YSZ-based sensor with a combination of $CuCrFeO_4$ and $CoCrFeO_4$ electrodes

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Abstract

A solid-state potentiometric sensor using yttria-stabilized zirconia (YSZ) as a solid electrolyte and oxide electrodes has been developed for selective CO detection. At 450°C, the YSZ-based sensor using $CuCrFeO_4$ sensing-electrode (SE) was found to have similar gas sensing characteristic with the sensor using $CoCrFeO_4$-SE, except toward CO. When both SEs was paired on a YSZ tube, the responses to various gases except for CO could be cancelled out for the resulting combined-SEs sensor. Thus, this sensor could generate a sensitive and selective response to CO at 450°C even under humid conditions.

Peer-review under responsibility of Universiti Malaysia Perlis

Keywords: CO sensor; Mixed potential; YSZ; $CuCrFeO_4$; $CoCrFeO_4$

1. Introduction

A solid-state potentiometric (mixed-potential type) sensor that is based on yttria-stabilized zirconia (YSZ) solid electrolyte attached with a metal oxide sensing-electrode (SE) has been considered promising for high-performance gas sensing. Normally, the sensing signal of the mixed-potential type sensor arises, when both of the cathodic reaction of O_2 and the anodic reaction of reducing gas that occur simultaneously at the interface of SE and YSZ reach a steady state. The balance among the catalytic activities of the electrode material toward the gas-phase and electrochemical reactions can govern the sensitivity generated by this sensor [1].

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Peer-review under responsibility of Universiti Malaysia Perlis
doi:10.1016/j.proche.2016.07.021

Up to this moment, there has not been many reports regarding the development of potentiometric YSZ-based sensors for sensitive detection of CO and it is even fewer for a sensitive and selective CO sensing [2]. The most effective method to obtain a selective response to CO that has been reported so far, is pairing two electrodes that can cancel-out the unwanted responses against the various interfering gases, except for a target CO gas [3-5].

2. Material and Methods

2.1. Fabrication of the sensor

A commercial open-end YSZ tube (8 mol.% Y_2O_3-doped ZrO_2, Nikkato, Japan, 300 mm in length; 5 and 8 mm in inner and outer diameter, respectively) was used as the base solid-electrolyte. Initially, an intermediate YSZ (*i*-YSZ) layer was fabricated to ensure a good attachment between SE and YSZ. The YSZ powder (8 mol.% Y_2O_3-doped ZrO_2, Tosoh, Japan) was mixed with an organic binder (α-terpineol) and the resulting paste was applied onto the surface of the YSZ tube to form the *i*-YSZ layer. To fabricate the SE layer, the oxide powders were mixed with α-terpineol and ground in a mortar. The obtained paste was applied onto the surface of the *i*-YSZ layer to form an SE layer. The YSZ tube attached with these layers was then dried at 100°C overnight, followed by firing at 1000°C in air for 2 h to obtain a final sensor.

2.2. Evaluation of the sensing characteristics

The fabricated YSZ-based sensor was assembled in a custom-made quartz cell which was connected to a conventional sensor-testing system equipped with a high-temperature electric furnace and a mass-flow controlling system. The sensor was exposed alternately to the humidified base gas (21 vol.% O_2 + H_2O + N_2 balance) or the humidified sample gas (CO, C_3H_8, C_3H_6, CH_4, NH_3, NO or NO_2, 100 ppm each, diluted with the base gas) at a constant gas flow-rate of 100 cm^3/min. The construction of the single-SE type sensor is presented in Fig. 1(a), where a single SE layer was attached onto the YSZ tube and was measured against Pt reference-electrode (RE). Pt-RE was formed on the inner side of the YSZ tube and was always exposed to an atmospheric air to construct Pt/air-RE. A combined-SEs type sensor (Fig. 1(b)) was comprised of two SEs attached on the surface of the YSZ tube and each of them was connected to the positive and negative side of the electrometer.

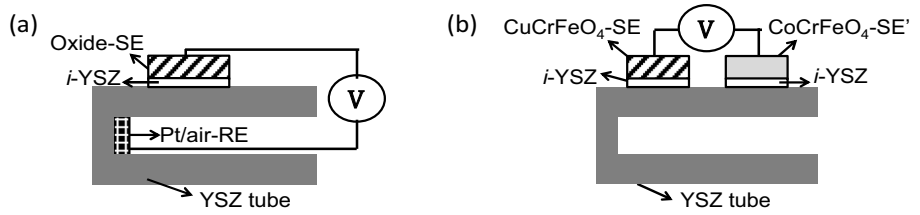

Fig. 1 The schematic construction of the single-SE-type (a) and the combined-SE-type (b) YSZ-based sensors.

3. Result and Discussion

Initially, the sensing characteristics of the single-SE type sensors attached with each of spinel-oxide SEs were examined at 450°C. The sensor using $CuCrFeO_4$-SE and Pt/air-RE was found to capable of detecting various gases, including CO. On the contrary, the sensor utilizing $CoCrFeO_4$-SE and Pt/air-RE

was capable of generating similar sensitivity toward various gases except for CO. These results suggest that, when both SEs are combined on a YSZ tube, the resulting sensor may be able to detect CO sensitively and selectively.

A combined-SEs type sensor was then constructed as illustrated in Fig. 1(b) by using both $CuCrFeO_4$ and $CoCrFeO_4$ electrodes, and its sensing characteristic was examined. The result given in Fig. 2 confirmed that the unwanted responses to various interfering gases (including hydrocarbon, NOx and NH_3) could be diminished by pairing $CuCrFeO_4$-SE and $CoCrFeO_4$-SE to construct a combined-SEs type sensor, while maintain the sensitive response to CO. This encouraging result requires further investigation regarding the sensing characteristics in more detail and the elucidation on its sensing mechanism of the developed sensor is also necessary.

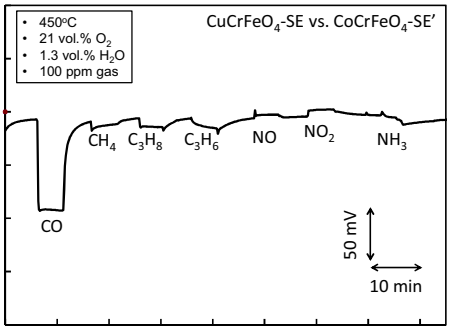

Fig. 2 Response curves to various gases for the YSZ-based sensor attached with both of $CuCrFeO_4$-SE and $CoCrFeO_4$-SE.

4. Conclusions

We have successfully developed a sensor that can detect CO sensitively and selectively by combining $CuCrFeO_4$ and $CoCrFeO_4$ as SE for the potentiometric YSZ-based sensor. This positive results show the potential of the developed sensor to function as a high-performance solid-state CO sensor.

Acknowledgement

This work was supported by JSPS KAKENHI Grant Number 25288109

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